Proceedings of the American Academy of Arts and Sciences

Vol. 72, No. 3—January, 1938

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 384.)

AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE. V.

THE REPRODUCIBILITY OF THE ICE POINT AND THE TRIPLE-POINT OF WATER. THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

By James A. Beattie, Tzu-Ching Huang, and Manson Benedict

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 384.)

AN EXPERIMENTAL STUDY OF THE ABSOLUTE TEMPERATURE SCALE. V.

THE REPRODUCIBILITY OF THE ICE POINT AND THE TRIPLE-POINT OF WATER. THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

By James A. Beattie, Tzu-Ching Huang, and Manson Benedict

Received February 1, 1937 Presented December 8, 1937

TABLE OF CONTENTS page

1. Introduction 137
2. Variables Affecting the Temperature of the Ice Point 138
3. Variables Affecting the Temperature of the Triple-Point of Water 142
4. Computation of the Temperature of the Triple-Point of Water 143
5. Measurement of the Temperature of the Triple-Point of Water 144
6. Summary 148

1. Introduction

The ice point, 0° C., is one of the fixed points on the absolute temperature scale and on the International Temperature Scale. It is defined as "the temperature at which pure, finely divided ice is in equilibrium with pure, air-saturated water under standard atmospheric pressure."[1] The reproducibility of the ice point has been questioned in recent years and the advisability of using the triple-point of water (the temperature at which pure ice, liquid water, and water vapor are in equilibrium) considered. The temperature of the ice point is lower than that of the triple-point of water by 0.00980° C., of which 0.00743° C. is due to the effect of pressure on the freezing point of pure water and the balance due to the freezing point depression resulting from the solution in water of the gases composing the atmosphere.

Moser[2] states that the ice point prepared according to the method given by Henning[3] is reproducible to 0.002 to 0.003° C.; he found that the temperature of the triple-point of water could be reproduced to $\pm 0.5 \times 10^{-4}$ °C.; and remained constant within this variation for

[1] See G. K. Burgess, Bur. Standards J. Research, *1*, 635 (1928).
[2] H. Moser, Ann. der Physik, (5) *1*, 341 (1929).
[3] F. Henning, "Temperaturmessung," p. 231; Vieweg (1915).

some days. He found that the temperature of equilibrium between ice and pure water is lowered $0.00748 \pm 0.00005°$ C. by an increase in pressure of 760 mm. This corresponds to a lowering of 0.00743° C. when the pressure is increased from 4.6 mm. of mercury (the triple-point vapor pressure) to 760 mm. He computed the effect of air saturating the water to be a further lowering of 0.0024° C., giving a total of 0.0098° C. for the difference between the ice point and the triple-point of water.

White[4] considered that the variations encountered in the ice point were due to impurities on the surface of the ice. He made 17 "cold cells"—closed vessels containing an ice-water mixture immersed in an ice bath—each with two outlets, one for introducing fresh water and the other for removal of the water in the cell. He found that when first prepared the temperatures of 14 of the cold cells differed by 0.001° C. or more; when, however, the water in the cold cells was replaced by fresh, air-saturated water cooled to 0° C., the temperatures of all of the cells could be brought to within 0.5 to 1.0×10^{-4}° C. of each other.

Thomas[5] was able to reproduce the ice point within 1.0 to 1.5×10^{-4} °C. over a period of months. He measured the difference between the ice point and the triple-point of water and obtained a value of 0.0097° C. at an average barometer reading of 750 mm.

2. Variables Affecting the Temperature of the Ice Point

Pressure. At a distance h mm. below the level of the water, the temperature t° C. of equilibrium between ice and water saturated with air at 0° C. and at a barometric pressure of p mm. of mercury is:

$$t = -0.00980\frac{p-760}{760} - \frac{0.00748 \times 0.999868}{760 \times 13.5955}h$$

$$= -1.29 \times 10^{-5}(p-760) - 0.072 \times 10^{-5}h \qquad (1)$$

The barometric correction is not negligible. In a place such as Denver, Colorado where the average atmospheric pressure is 630 mm., the barometric correction amounts to 17×10^{-4} °C. The maximum variation in atmospheric pressure at Cambridge, Massachusetts amounts to about 40 mm., which corresponds to a variation of 5×10^{-4} °C. in the temperature in an ice point cell.

A depth of immersion of a thermometer in an ice point cell of 15 cm. necessitates a correction of -1×10^{-4} °C.

---

[4] W. P. White, J. Am. Chem. Soc., *56*, 20 (1934).

[5] J. L. Thomas, Bur. Standards J. Research, *12*, 323 (1934).

Purity of Ice and Water. The specific conductances of water obtained from several sources are given in Table I. All conductances were determined at 10° C.,[6] and it was assumed that no CO_2 was lost or gained by the water during the short time required to make the measurement. The corresponding freezing point depression $-\Delta t$ was *computed* from the equation

$$-\Delta t = 2 \times 1.858 \times 1000\,(L - L')\,/\Lambda_0 \qquad (2)$$

where 1.858 is the limiting molal freezing-point depression of water, L and L' are, respectively, the specific conductance of the sample of water and that of pure water saturated with air at 0° C. and 760 mm. total pressure, and Λ_0 is the limiting equivalent conductance of the impurity. We assumed that the impurity was sodium chloride for which Λ_0 has the value 67 ohms^{-1} at 0° C. and 89 at 10° C. The specific conductance of water saturated with air at 0° C. and 760 mm. is 0.7×10^{-6} when measured at 0° C. and 0.9×10^{-6} when measured at 10° C. (See Table II.) Thus

$$-\Delta t = 55(L - 0.7 \times 10^{-6}) \quad \text{(when } L \text{ is measured at 0° C.)} \qquad (3)$$

$$-\Delta t = 42(L - 0.9 \times 10^{-6}) \quad \text{(when } L \text{ is measured at 10° C.)} \qquad (4)$$

The data given in Table I show clearly that the impurities in the different kinds of water and ice,[7] the raw materials of an ice point cell, account for a variation in temperature of only 0.4×10^{-4} °C. The introduction of the impurities must take place in the preparation of the cell, as suggested by White;[4] and this is shown by the data on the ice point cells A and B. In the preparation of both cells ordinary precautions to prevent the introduction of impurities were taken. Clear ice cut into pieces about 12 cm. on a side, were rinsed with distilled water, and shaved into a fine snow by means of a commercial motor-driven shaver. The ice point cell (a silvered Dewar tube), the stainless-steel stirring rod and the case of the thermometer were rinsed with distilled water and allowed to drain. For cell A the shaved ice was transferred to the Dewar tube by the bare hands which had been rinsed with distilled water; for cell B the ice was transferred by

[6] We wish to thank Professor George Scatchard and Miss Marjorie Allen (now Mrs. Manson Benedict) for making the conductance measurements. The method was that of G. Scatchard, P. T. Jones, and S. S. Prentiss, J. Am. Chem. Soc., *54*, 2676 (1932).

[7] For the determination of the specific conductances of water obtained from melted ice, a single piece of the ice was washed, melted and the specific conductance measured without any attempt to air-saturate the water. This operation corresponds to what takes place in an ice point cell.

means of a glass vessel. The water, which was added to the cell in sufficient quantity to make a mush that was easily stirred, had been stored for 12 hours in an unstoppered pyrex bottle in an ice-chest, whereby its temperature fell to 5° C., and immediately before use had been cooled to 0° C. by the addition of pieces of washed ice about 2 cm. on a side, and air-saturated by frequent vigorous shaking for a period of one-half hour. After the thermometer had been inserted, the ice-water mixture was stirred by raising and lowering the stirring-rod which had a loop in a horizontal plane, and the ice pressed down until a few millimeters of water showed above the surface of the ice. In the preparation of cell A the ice was transferred to the ice point cell by the bare hands which had been rinsed with distilled water; sufficient impurity was thereby introduced to lower the temperature by a computed amount of 6 to 10×10^{-4} °C. In the preparation of cell B the ice was transferred by means of a glass vessel; the computed freezing point lowering due to impurity was 1 to 2×10^{-4} °C. In each case the same spread of values occurred whether the cell was filled with commercial or distilled-water ice and distilled water, or with conductivity-water ice and conductivity water.

When the water in either cell A or cell B was renewed three times with conductivity water according to the method of White,[4] the computed correction for impurity fell to 0.2 to 0.3×10^{-4} °C., approximately the value for the water added.

Saturation of the Water with Air. In Tables II and III are given the details and in Table IV a résumé of the results of the calculation of the specific conductances, the composition, and the freezing points of solutions saturated with air at various temperatures and pressures. The computations are based on the ideal-gas law, Dalton's law, Henry's law, and the laws of ideal solutions, and should not be in error by more than 0.5% due to these assumptions. The CO_2 content of laboratory air has been determined on three different occasions, the values falling between 0.034 and 0.036 mol per cent.

Barometric pressure is not under our control but it is always possible to cool the water used in making an ice point cell to 0° C. and saturate it with air. From Table IV it will be seen that when water saturated with air at 25° C. is used a maximum error of 10×10^{-4} °C. may result; if saturated at 5° C., an error of 3×10^{-4} °C.

Conclusion. The temperature t° C. in an ice point cell is given by the relation:

$$t = -1.29 \times 10^{-5}(p - 760) - 0.072 \times 10^{-5}h - 42 \qquad (L - 0.9 \times 10^{-6}) \quad (5)$$

where the water used in the cell has been saturated with air at 0° C. and a barometric pressure of p mm., h is the distance below the surface of the water in mm., and L is the specific conductance in ohms^{-1} cm.$^{-1}$ of the water in the cell measured at 10° C. If L is measured at 0° C. the last term of Eq. (5) should read $55\,(L - 0.7 \times 10^{-6})$. The conductance correction is uncertain to 10% and hence should not exceed 5×10^{-4} °C. ($L = 13 \times 10^{-6}$).

When the corrections and implications of Eq. (5) are not taken into consideration, the variations in the indicated temperatures in an ice point cell may be of the order of: (a) 5×10^{-4} °C. for variations in the barometric pressure, (b) 1×10^{-4} °C. for variations in depth of immersion of thermometer, (c) 10×10^{-4} °C. for impurities introduced in shaving the ice, and (d) 10×10^{-4} °C. for lack of saturation of the water with air at 0° C.: a total of about 25×10^{-4} °C. In addition there may be a constant error as large or larger than this value due to conditions which, though fairly constant, deviate considerably from standard. A constant temperature in the ice point cell is no guarantee that the temperature is 0° C.

A second cause of variation in the indicated temperature of the ice point may be in the thermometer itself. The ice point resistance of a well constructed and properly annealed platinum resistance thermometer has changed by an amount equivalent to 10×10^{-4} °C. at the ice point when heated to the sulphur boiling point for as short a time as twelve hours; whereas when used continually at the steam point for three months the ice point resistance has changed by an amount equivalent to 5×10^{-4} °C. These effects were not due to variation in the temperature in the ice point cell but to real changes in the properties of the thermometer.

Our experience extending over a period of many years with the reproducibility of temperature in ice point cells is summarized in Table V. Method 6 was used for the experimental portion of the work described in the present paper. Method 3, 4, or 5 is used at present for the determination of the ice point of platinum resistance thermometers; in all three the temperature is constant within the precision of the thermometry. Methods 1 and 2 were used previously. Occasionally an indicated ice point will drop by as much as 50×10^{-4} °C.; such a change is always correlated with a very positive test for chlorides in the distilled water used.

When care is used in preparing an ice point cell and when the proper corrections are applied, the ice point can be reproduced to 0.5×10^{-4} °C.

3. Variables Affecting the Temperature of the Triple-Point of Water

Pressure. A triple-point cell can be filled with water so free from dissolved air that the pressure of the residual permanent gases is entirely negligible. The lowering of temperature $-\Delta t°$ C., of equilibrium between ice and water at a distance H mm. below the surface of the water is

$$-\Delta t = 0.072 \times 10^{-5} H. \tag{6}$$

Purity of the Ice and Water. There should be no dissolved CO_2 in a properly filled triple-point cell. The ice, frozen in the cell, should be of exceptional purity. There is however always some impurity in the water and this increases slowly with time due to solution of the components of glass. Moser[2] found that the specific conductance at 18° C. of the water in a triple-point cell was 0.3×10^{-6} ohms^{-1} cm.$^{-1}$ at the end of several days and after several months the specific conductance was 0.7×10^{-6} when the cell was made of Jena 59^{III} glass and 1.5×10^{-6} when of 16^{III} glass. In our cell, which was made of pyrex glass, the water had a specific conductance of 0.7×10^{-6} at 10° C. after two months for one filling and 0.8×10^{-6} after two months for another filling. After the third filling the cell was not opened until twenty months had elapsed, when the specific conductance was found to be 0.8×10^{-6}. This result seems to indicate that the impurity present is not due to the progressive solution of the glass. We shall assume the impurity to have the same effect as sodium chloride.

The lowering of the temperature, $-\Delta t°$ C., of the triple-point due to impurities in the water is

$$-\Delta t = 42(L - 0.02 \times 10^{-6}), \tag{7}$$

where L is the specific conductance of the water in the cell measured at 10° C. and 0.02×10^{-6} is the specific conductance of pure water (negligible). For a specific conductance of 0.7 to 0.8 $\times 10^{-6}$ the correction is -0.3×10^{-4} °C.

Thickness of the Ice Film. Neither Moser nor we found any measurable effect due to the thickness of the ice film.

Radiation and Conduction. It is usual practice to fill the re-entrant tube of the triple-point cell with mercury in order to increase heat transfer to the thermometer. Heat leaking downward along the thermometer can be made negligible by immersing the entire triple-point tube and part of the thermometer stem in an ice bath.

We found a slight effect, about 0.3×10^{-4} °C., due to radiation. This was eliminated by wrapping the ice bath around the triple-point cell with aluminum foil.

Conclusion. The temperature $t°$ C. in a triple-point cell is:

$$t = 0.00980 - 0.072 \times 10^{-5} H - 42L \tag{8}$$

where 0.0098° C. is the triple-point temperature of water, H the distance below the surface of the water in mm. and L the specific conductance of the water in the cell, measured at 10° C. The conductance correction is uncertain to 30% and hence should not exceed 1.5×10^{-4} °C. ($L = 4 \times 10^{-6}$).

The experience of Moser[2] and ourselves shows that it is a relatively easy matter to fill a triple-point cell with water by distillation in vacuo so that the residual air has a negligible effect from the standpoint both of pressure and its solution in the water. When proper glasses are used in the construction of the cell, the specific conductance of the water is below 1×10^{-6} after twenty months, which corresponds to a correction of -0.4×10^{-4} °C.

Under proper conditions the triple-point of water can be reproduced to 0.5×10^{-4} °C.

4. Computation of the Temperature of the Triple-Point of Water

If we assume that the effect of pressure and of the air dissolved in the water act independently, the computation of the temperature of the triple-point of water is readily made. The effect of an increase of pressure from the triple-point pressure (4.6 mm.) to 760 mm. can be evaluated from the Clapeyron equation:

$$\Delta t = T(v_w - v_i)\Delta p/\Delta H$$

$$= \frac{273.16\,(1.00013 - 1.09075)\,755.4 \times 1.01325 \times 10^6}{333.6 \times 10^7 \times 760}$$

$$= -0.00747° \text{ C.} \tag{9}$$

where the uncertainty is 0.5×10^{-4} °C. due to the uncertainty in the density of ice, 0.9168 ± 0.0005 gms. per milliliter, and in the heat of fusion of ice, 333.6 ± 0.33 joules per gram.[8] The value obtained by Moser[2] is $-0.00743 \pm 0.00005°$ C. The effect of saturation of the water with air at a total pressure of one atmosphere is

$$\Delta t = -1.858 \times 0.001313 = -0.00244° \text{ C.} \tag{10}$$

[8] International Critical Tables, Vol. 3, p. 43 (1928); and Vol. 5, p. 131 (1929).

where the value 0.001313 comes from Table III. The uncertainty is 0.3×10^{-4} °C.

Thus the computed value of the triple-point temperature of water is $+ 0.0099 \pm 0.0001°$ C.

5. Measurement of the Temperature of the Triple-Point of Water

The Apparatus. A sketch of the apparatus is shown in Fig. 1. The 48 junction copper (No. 36) constantin (No. 30) thermocouple *A* was divided into 8 groups of 6 junctions each similar to that of Scatchard, Jones, and Prentiss.[6] The binding posts were of copper. The wires were enclosed in a vacuum-tight nickel case filled with dry nitrogen at one atmosphere pressure. The wires were from the same spools as those used by Scatchard and Benedict,[9] and we employed their equation for converting electromotive force into temperature:

$$\Delta t° \text{ C.} = 5.37931 \times 10^{-4}E + 0.2905 \times 10^{-9}E^2 + 0.1413 \times 10^{-14}E^3 + 0.141 \times 10^{-18}E^4 \qquad (11)$$

where E is in microvolts. We checked this equation for our thermocouple to 0.03% for temperature differences of 2.8 to 3.8° C. by replacing the triple-point cell with one similar to the ice point cell filled with shaved ice and a sodium chloride solution. The calibration was made against a platinum resistance thermometer in the manner described by Scatchard, Jones, and Prentiss.[6]

The triple-point cell *B* was similar to that used by Moser.[2] It was made of pyrex glass. The thermocouple was inserted into the reentrant tube through a rubber stopper and was surrounded by mercury for a distance of 15.5 cm. The cell was steamed out for ten hours, boiled with a 1 : 1 mixture of concentrated sulphuric and nitric acids, and rinsed many times with distilled and conductivity water. It was sealed in an inverted position to the filling apparatus which contained no stopcocks. Conductivity water was treated with barium hydroxide and the solution poured into the first of two distilling flasks which formed part of the filling apparatus. The water was distilled to the second flask through a spray trap with violent boiling, the system being evacuated by means of a mercury diffusion pump protected by two water traps, the second immersed in liquid air. The first flask was sealed off from the system and the water distilled more slowly into the triple-point tube. In the final distillation

[9] G. Scatchard and M. Allen Benedict, J. Am. Chem. Soc., *58*, 837 (1936).

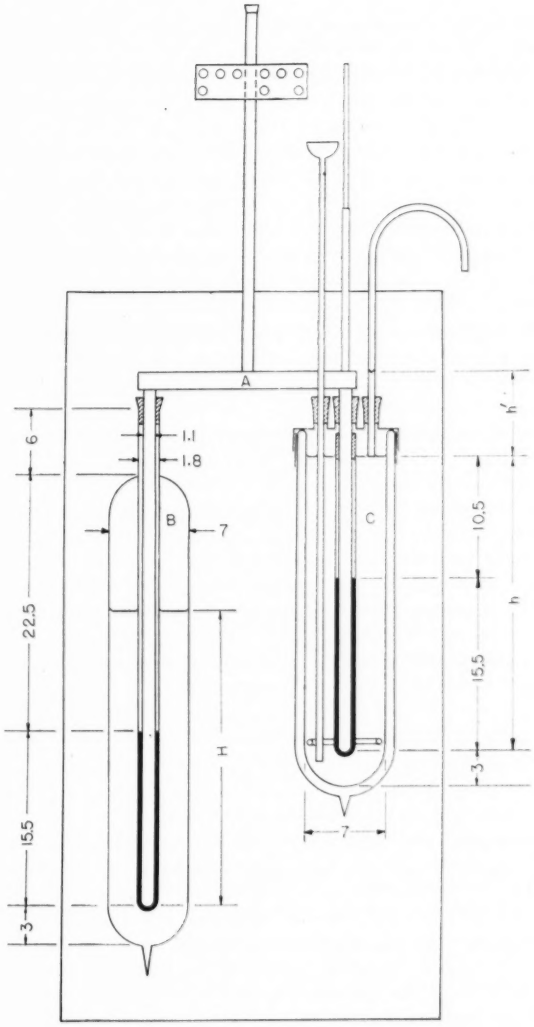

FIG. 1.—Sketch of the apparatus. Dimensions are in centimeters.

the pressure read near the diffusion pump did not exceed 10^{-4} mm. of mercury. Three separate fillings of the cell were made. For the first two the specific conductances of the water after two months was 0.7 to 0.8 $\times$ 10^{-6} ohms^{-1} cm.$^{-1}$; for the third, the specific conductance of the water after twenty months was 0.8 $\times$ 10^{-6}.

The ice point cell *C* was a silvered pyrex Dewar tube fitted with a brass top made water-tight by rubber tape. The top carried four brass tubes through which were inserted: one arm of the thermocouple, a tube for the introduction of water, a tube for the removal of water, and a tube carrying a glass stirrer (shown behind the thermocouple in Fig. 1). The exit tube and the tube carrying the stirrer projected below the top so that the water in the cell did not come in contact with the metal. The arm of the thermocouple was surrounded by a glass tube from the same piece as the re-entrant tube of the triple point cell, the annular space being filled with mercury for a distance of 15.5 cm.

The entire apparatus was immersed in a bath of cracked commercial ice (1 cm. on a side) and distilled water. The large glass vessel was covered with aluminum foil.

The Measurements. The triple-point cell was placed in an ice bath and a long glass tube slightly smaller in diameter than the arm of the thermocouple inserted into the mercury well. Liquid ammonia was blown into the tube until a layer of ice ⅛ to ¼ inch was frozen around the re-entrant tube. When the surface of the mercury is at the same level as that of the water, super-cooling occurs; when the mercury surface is below that of the water, the freezing proceeds more smoothly.

The ice point cell was filled with a mixture of shaved ice and conductivity water. The water was stored in an ice-chest overnight, and just before use was cooled to 0° C. by the addition of pieces of washed ice about 2 cm. on a side and saturated with air by frequent vigorous shaking over a period of one-half hour.

The apparatus was assembled and surrounded by an ice-water mixture. After about one-half hour measurement of the electromotive force of the thermocouple was begun. We found no difference within 0.2 $\times$ 10^{-4} °C. between the values obtained when the mixture in the ice point cell was stirred continuously or when stirred for 30 seconds, the stirring stopped, and the reading made immediately afterwards. When the mixture was not stirred over a period of five minutes the temperature was high by about 0.5 $\times$ 10^{-4} °C. which may be within the experimental error. We adopted the method of intermittent stirring for all of our measurements.

In each run from 6 to 15 readings of electromotive force were made; the water in the ice point cell replaced by pouring air-saturated water cooled to 0° C. down the thistle tube and another set of electromotive force readings made; and this process repeated three or four times. The water removed from the cell was stored in stoppered flasks immersed in ice for the determination of specific conductance which was measured at 10° C., as described in Section 2.

After the completion of two series of runs the triple-point cell was opened and the specific conductance of the water at 10° C. immediately determined. In the case of Run 5 the cell was not opened until twenty months after the completion of the measurements.

Corrections. Each arm of the thermocouple is surrounded by mercury in the same manner, so that it is proper to measure distances of immersion from the bottom of the arm in each cell. The temperature t_{ic} in the ice point cell is

$$t_{ic} = -1.29 \times 10^{-5}(p - 760) - 0.072 \times 10^{-5}(h + h') - 42(L_{ic} - 0.9 \times 10^{-6}); \quad (12)$$

and the temperature t_{tc} in the triple point cell is

$$t_{tc} = t_{tp} - 0.072 \times 10^{-5} H - 42 L_{tc} \quad (13)$$

where p is the barometric pressure at which the water was air-saturated, h, h', and H are heads of water in mm. (see Fig. 1), L_{ic} and L_{tc} are the specific conductances at 10° C. of the water in the ice point cell and triple-point cell, respectively, and t_{tp} is the true triple-point temperature of water.

Let Θ be the measured temperature difference $t_{tc} - t_{ic}$. Then

$$t_{tp} = \Theta - 1.29 \times 10^{-5}(p - 760) - 0.072 \times 10^{-5}(h + h' - H) - 42(L_{ic} - 0.9 \times 10^{-6} - L_{tc}). \quad (14)$$

Data. The data are given in Table VI. Three fillings of the triple-point tube were made. For the third, the specific conductance of the water was taken to be the same as for the second, since this cell was not opened until twenty months after the experimental work was completed. In the third, fourth, and fifth runs the specific conductance of the water from the ice point cell was not determined for every renewal, since the values all lay between 1.3 and 1.4×10^{-6} ohms^{-1} cm.$^{-1}$.

The final value for the triple-point of water is 0.00980 ± 0.00005° C.

6. Summary

The temperature $t°$ C. in an ice point cell at a distance h mm. below the surface of the water is:

$$t° \text{ C.} = -1.29 \times 10^{-5}(p - 760) - 0.072 \times 10^{-5}h - 42(L - 0.9 \times 10^{-6}),$$

where the water used in preparing the cell has been saturated with air at 0° C. and a barometric pressure of p mm. and L is the specific conductance of the water measured at 10° C. The saturation of the air at 0° C. and the application of the corrections for barometric pressure and depth are necessary if errors of the order of 0.002° C. are important. The conductance correction is uncertain to 10% and should be kept small. With some care in the preparation of the cell and when the corrections for barometric pressure and depth of immersion are applied, temperatures reproducible to 3×10^{-4} °C. can be obtained; when the White method of replacing the water in the cell is used the reproducibility is 0.5×10^{-4} °C.

The temperature $t°$ C. in a triple-point cell at a distance H mm. below the surface of the water is:

$$t° \text{ C.} = 0.00980 - 0.072 \times 10^{-5}h - 42L$$

where $0.00980 \pm 0.00005°$ C. is the triple-point temperature of water and L the specific conductance of the water in the cell measured at 10° C. The conductance correction is uncertain to 30%. The temperature in a triple-point cell can be reproduced to 0.5×10^{-4} °C. The specific conductance of the water from a pyrex glass cell was 0.7×10^{-6} and 0.8×10^{-6} ohm^{-1} cm.$^{-1}$ after two months for two separate fillings and 0.8×10^{-6} after twenty months for a third filling.

The computed value of the triple-point of water is $0.0099 \pm 0.0001°$ C., the measured value is $0.00981 \pm 0.00005°$ C.

Cambridge, Massachusetts.

TABLE I

CONDUCTANCE OF WATER FROM VARIOUS SOURCES AND CORRESPONDING COMPUTED FREEZING POINT LOWERING DUE TO IMPURITIES

$-\Delta t$ = Freezing point lowering = $42\ (L - 0.9 \times 10^{-6})$

Source of water	Spec. Cond. at 10° C.	Freezing Pt. Lowering
	$L \times 10^6$, $ohms^{-1}\ cm.^{-1}$	$-\Delta t \times 10^4$, °C.
Conductivity water fresh from still	0.7	
Conductivity water air-saturated at 0°C.	1.3	0.2
Melted conductivity-water ice	0.9	
Distilled water from tap	1.4	
Distilled water air-saturated at 0°C.	1.6	0.3
Melted distilled-water ice	1.5	
Melted commercial ice	2.0	
Water from ice point cell A	15–25	6–10
Water from ice point cell B	4–6	1.3–2.1
Water from cell A or B after third renewal with conductivity water	1.3–1.5	0.2–0.3

All water used in ice point cells was air-saturated at 0° C. The specific conductance of pure water air-saturated at 0° C. is $0.9 \times 10^{-6} ohms^{-1} cm.^{-1}$ at 10° C. (on the assumption that no CO_2 is lost).

Calculations of freezing point lowering are based on assumption that all impurity is sodium chloride for which equivalent conductance at zero concentration is 89 $ohms^{-1}$ at 10° C.

In the preparation of cell A the ice was handled with the bare hands; for cell B the ice never came in contact with the hands. The same spread of conductances occurred whether the cells were made of commercial ice or distilled-water ice and distilled water, or of conductivity-water ice and conductivity water.

TABLE II

Specific Conductances of Water Saturated with Air at Various Temperatures

p_{CO_2} (mm.) = 0.00035 (760 − p_w).

$$[H_2CO_3] = \frac{1000}{18.0154\left[\frac{K}{p_{CO_2}} - 1\right]}.$$

$$[H^+] = [HCO_3^-] = \sqrt{[H_2CO_3] \times K_1}\ .$$

$$\gamma = \sqrt{K_1(1-\gamma)/[\text{Total } CO_2]}\ .$$

L (Specific conductance, ohms^{-1}cm.$^{-1}$) = $L_w + \Lambda_0[HCO_3^-]/1000$.

p_w = vapor pressure of water (mm.).

K = p_{CO_2} (mm.)/mol fraction H_2CO_3 in solution.

K_1 = first ionization constant of H_2CO_3.

100γ = % ionization when t is changed to 10° C. without gain or loss of CO_2. K_1 is for 10° C. and [Total CO_2] is for t° C.

L_w = sp. cond. of pure water at t° C.

Λ_0 = limiting equivalent conductance of H_2CO_3 at t° C.

Temp.	p_{CO_2}	$K\times10^{-6}$[a]	$K_1\times10^7$[b]	Λ_0[b]	$L_w\times10^6$	$[H_2CO_3]$	$[H^+] = [HCO_3^-]$	[Total CO_2]	[Total Solute]	% Ionization	$L\times10^6$	When t is changed to 10° C. without gain or loss of CO_2.	
t° C.	mm.					mols × 10^6/1000 gms. water						100γ	$L\times10^6$
0	0.264	0.5526	2.61	248	0.01	26.5	2.63	29.1	31.8	9.0	0.66	10.2	0.93
5	.264	0.6663	3.00	278	.02	22.0	2.57	24.6	27.1	10.4	.73	11.1	.86
10	.263	0.7915	3.38	307	.02	18.4	2.49	20.9	23.4	11.9	.78	11.9	.78
25	.258	1.243	4.31	394	.06	11.5	2.23	13.7	16.0	16.3	.94	14.5	.63

[a] Bohr, see International Critical Tables, Vol. 3, p. 260 (1928).

[b] T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc., *57*, 1705 (1935).

TABLE III

Composition of Water Saturated with Air at Various Temperatures

Composition of dry air[a]: 78.025 mol % N_2, 20.99 mol % O_2, 0.94 mol % A, 0.01 mol % H_2, 0.035 mol % CO_2

p_A(mm.) = 0.01 × mol % A(760 − p_w). p_w = vapor pressure water (mm.).

$$\text{Mols A/1000 gms. water} = \frac{1000}{18.0154\left(\frac{K_A}{p_A(\text{mm.})} - 1\right)} \qquad K_A = p_A \text{ (mm.)/mol fraction A in solution.}$$

Gas	Partial Pressures (mm.) in air saturated with water vapor at $t°$ C.				Reference	Henry's Law Constant $K \times 10^{-7}$[b]				Moles Solute × 10^6 per 1000 gms. water at $t°$ C.			
	0°	5°	10°	25°		0°	5°	10°	25°	0°	5°	10°	25°
H_2O	4.59	6.55	9.21	23.75									
N_2	589.41	587.88	585.80	574.46	W	4.089	4.609	5.168	6.686	800	708	629	477
					F	4.077	4.572	5.074	6.435	802	714	641	496
O_2	158.56	158.15	157.59	154.54	W	1.934	2.205	2.486	3.314	455	398	352	259
					F	1.921	2.190	2.460	3.265	458	401	356	263
A	7.10	7.08	7.06	6.92	W	1.79	2.02	2.25	2.92	22	19	17	13
					E	1.635	1.861	2.089	2.708	24	21	19	14
H_2	.08	.08	.08	.07	W	4.401	4.623	4.834	5.374	0	0	0	0
					T	4.391	4.587	4.778	5.296	0	0	0	0
CO_2	.264	.264	.263	.258	See Table II					32	27	23	16
								Total (W)		1309	1152	1021	765
								Total (F, E, T)		1316	1163	1039	789
								Total (Average)		1313	1158	1030	777

[a] International Critical Tables, Vol. 1, p. 393 (1926). Values adjusted for 0.035 mol % CO_2.

[b] International Critical Tables, Vol. 3, p. 255 (1928). W = Winkler; F = Fox; T = Timofeev; E = Estreicher.

TABLE IV

FREEZING POINT OF WATER SATURATED WITH AIR AT VARIOUS TEMPERATURES AND AT A TOTAL PRESSURE OF 760 MM.

Total mols solute/1000 gms. water air-saturated at total pressure $p = 760$ mm. are given in Table III

$\Theta°$ C. = freezing point of solution = 1.858 (0.001313 − total mols solute/1000 gms. water).

Specific conductances are from Table II

Temp. of Saturation of water with air	Total Mols of solute at $p = 760$ mm.	Freezing Point ($p = 760$ mm.)	Specific Conductance of solution at 10° C.
$t°$ C.	mols/1000 gms. water	$\Theta°$ C.	ohms^{-1}cm.$^{-1}$
(1)	(2)	(3)	(4)
0	0.001313	0.0	0.9×10^{-6}
5	.001158	+0.00029	0.9×10^{-6}
10	.001030	+ .00053	0.8×10^{-6}
25	.000777	+ .00100	0.6×10^{-6}

Note: When the water is air-saturated at p mm. instead of 760 mm.:

$$\text{Total mols solute/1000 gms. water} = \frac{p - p_w}{760 - p_w} \times \text{value for 760 mm.}$$

Because of the slight effect of the ionization of H_2CO_3 this equation holds to the number of places given in column (2) of the above table.

TABLE V

OBSERVED VARIATIONS IN ICE POINT CELLS

Barometric correction (°C.) $= -1.29 \times 10^{-5}(p - 760)$. p = barometric pressure in mm.
Immersion correction (°C.) $= -0.072 \times 10^{-5} h$. h = depth of immersion in mm.
Conductance correction (°C.) $= -42(L - 0.9 \times 10^{-6})$. L = specific conductance ohms^{-1} cm.$^{-1}$ of water from cell measured at 10° C.

Method	Preparation of Ice Point Cell					Corrections Applied			Spread from maximum to min. temp. $\Delta t \times 10^4$ °C.
	Ice	Water	Handling of ice	Air-Saturation of water at 0° C.	Replacement of water in cell	Barometric	Immersion	Conductance	
1	Commercial	Distilled	By hand	no	no	no	no	no	30
2	Commercial	Distilled	By vessel	no	no	no	no	no	15
3	Distilled water	Distilled	By vessel	yes	no	no	yes	no	5
4	Distilled water	Distilled	By vessel	yes	no	yes	yes	no	3
5	Distilled water	Distilled	By vessel	yes	yes	yes	yes	no	1
6	Conductivity water	Conductivity	By vessel	yes	yes	yes	yes	yes	0.5

TABLE VI

The Temperature of the Triple-point of Water

I. P. = ice point. T. P. = triple-point.

H = distance from bottom of thermocouple tube to water level in T. P. cell (see Fig. 1).

$h + h'$ = distance from bottom of thermocouple tube to water level in I. P. cell (see Fig. 1).

Preparation of I. P. Cell	No. of Readings	E. M. F.	Θ	H	h	h'
		microvolts	°C. $\times 10^6$	mm.	mm.	mm.
(1)	(2)	(3)	(4)	(5)	(6)	(7)
	Run 1	First filling of triple-point cell.				
Orig. filling	15	19.61	10549	220	260	70
1st renewal	15	18.57	9989	220	260	70
2nd renewal	10	18.47	9936	220	260	70
3rd renewal	13	18.65	10032	220	260	70
	Run 2	First filling of triple-point cell.				
Orig. filling	6	18.95	10194	220	260	130
1st renewal	9	18.52	9962	220	260	0
2nd renewal	8	18.62	10016	220	260	110
3rd renewal	16	18.51	9957	220	260	90
	Run 3	Second filling of triple-point cell.				
1st renewal	6	18.18	9780	260	260	50
2nd renewal	7	18.23	9806	260	260	50
3rd renewal	6	18.33	9860	260	260	50
4th renewal	7	18.28	9833	260	260	50
	Run 4	Second filling of triple-point cell.				
1st renewal	6	18.14	9758	260	260	0
2nd renewal	6	18.26	9823	260	260	0
3rd renewal	8	18.19	9785	260	260	0
4th renewal	8	18.03	9699	260	260	0
	Run 5	Third filling of triple-point cell.				
1st renewal	6	18.27	9828	260	260	20
2nd renewal	7	18.15	9763	260	260	20
3rd renewal	7	18.16	9769	260	260	20
4th renewal	7	18.06	9715	260	260	20

TABLE VI—*Continued*

THE TEMPERATURE OF THE TRIPLE-POINT OF WATER

Θ °C. = 0.00053793 E.
Correction for static head (°C.) = $-$ 0.000 000 72 ($h + h' - H$).
Correction for barometric pressure (°C.) = $-0.000\,0129$ (p -760).
p = barometric pressure in mm.
Correction for conductance (°C.) = -42 ($L_{ic} - 0.9 \times 10^{-6} - L_{tc}$).

Bar.	Specific Conductance at 10° C.		Corr. for static head	Corr. for barometer	Corr. for conductance	Temp. of triple-point
	I. P. Cell	T. P. Cell				
mm.	$L_{ic}\times10^6$	$L_{tc}\times10^6$	°C. $\times 10^6$	°C. $\times 10^6$	°C. $\times 10^6$	°C.
(8)	(9)	(10)	(11)	(12)	(13)	(14)
	Commercial ice and conductivity water in ice point cell.					
767.0	15.0	0.7	−79	−90	−563	0.00982
767.0	1.5	0.7	−79	−90	+ 4	.00982
767.0	1.5	0.7	−79	−90	+ 4	.00977
764.7	2.6	0.7	−79	−61	−42	.00985
	Conductivity ice and conductivity water in ice point cell.					
767.2	6.0	0.7	−122	−93	−185	.00979
767.2	1.5	0.7	− 29	−93	+ 4	.00984
767.2	1.5	0.7	−108	−93	+ 4	.00982
767.2	1.5	0.7	− 94	−93	+ 4	.00977
	Conductivity ice and conductivity water in ice point cell.					
761.0	1.3	0.8	−36	−13	+17	.00975
760.7	1.3	0.8	−36	− 9	+17	.00978
760.5	1.3	0.8	−36	− 6	+17	.00984
760.5	1.3	0.8	−36	− 6	+17	.00981
	Conductivity ice and conductivity water in ice point cell.					
756.6	1.4	0.8	0	+44	+13	.00982
757.0	1.4	0.8	0	+39	+13	.00988
757.0	1.3	0.8	0	+39	+17	.00984
757.0	1.3	0.8	0	+39	+17	.00976
	Conductivity ice and conductivity water in ice point cell.					
756.2	1.4	0.8	−14	+49	+13	.00988
756.2	1.4	0.8	−14	+49	+13	.00981
755.8	1.4	0.8	−14	+54	+13	.00982
755.6	1.4	0.8	−14	+57	+13	.00977
					Average	.00981
						±0.00003